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Atrazine, Deethylatrazine, and Deisopropylatrazine in Surface Runoff from Conservation Tilled Watersheds

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Atrazine and two of its metabolites, deethylatrazine (DEA) and deisopropylatrazine (DIA), are frequently detected in surface runoff. Although their health and environmental effects may be similar to that of atrazine and ratios of their concentrations are useful in delineating sources of contamination, there have been few long-term studies of the factors affecting their losses in runoff. Therefore, losses of atrazine, DEA, and DIA were monitored for six years in runoff from seven small (0.45−0.79 ha) watersheds under three tillage practices. Weather year and the timing of runoff-producing rainfall had a greater effect on atrazine, DEA, and DIA concentrations and losses than did tillage practice. DEA was the most frequently detected metabolite with an average concentration in the year of atrazine application, of 2.5 μg L^{-1} compared to 0.7 μg L^{-1} for DIA. Atrazine exceeded its 3 μg L^{-1} maximum contaminant level (MCL) up to 100 days after application. DEA and DIA exceeded the atrazine MCL up to 50 days after atrazine application; thus, failure to monitor their presence may result in underestimation of the environmental impact of atrazine usage. The molar concentration ratio of DEA to atrazine (DAR) was affected by tillage treatment, weather year, and possibly soil type. These factors may need to be taken into account when DAR is used as an index of atrazine movement. The ratio of DIA to DEA (D^2R) was fairly constant and should be useful in determining the parent compounds contributing DIA to surface waters.

Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) is one of the most widely used herbicides in North America and is primarily used for weed control during the production of corn with lesser amounts used on sorghum, sugarcane, and other crops (*1*). In the United States, conservation tillage practices must be used by farmers that grow corn on highly erodible land and want to maintain eligibility for commodity support payments. Conservation tillage being defined as any sequence of tillage operations designed to reduce losses of soil and water, generally by maintaining 30% or greater residue cover on the soil surface (*2*).

Atrazine is often used to produce corn in conservation tillage systems, and most natural rainfall studies indicate that conservation tillage reduces losses of water and atrazine in surface runoff compared to conventional (< 30% residue cover) tillage (*1*). Nevertheless, in many surveys, atrazine is the most frequently detected herbicide contaminant in surface water, groundwater, and rainfall in the Corn Belt region of the United States (*3*, *4*). Concern over this widespread usage and contamination has led to a large number of studies on the environmental fate of atrazine and its ecological risks (*1*, *5*). These studies generally indicate a low level of risk associated with typical exposures of 5 μg L^{-1} in aquatic ecosystems. Recently, however, laboratory and field studies suggest that atrazine concentrations as low as 0.1 μg L^{-1} can affect the sexual development of frogs. This has led to speculation that atrazine and other endocrine disruptors may be contributing to the worldwide decline in amphibian populations (*6*, *7*).

Another concern related to atrazine usage is widespread detection of its metabolites in streams throughout the Corn Belt (*8*). Two of the breakdown products of atrazine, deethylatrazine (DEA; 2-amino-4-chloro-6-isopropylamino-*s*-triazine) and deisopropylatrazine (DIA; 2-amino-4-chloro-6-ethylamino-*s*-triazine), are structurally and toxicologically similar to the parent compound (*3*). These metabolites are more mobile than atrazine, and their ecological risks should be similar and might be additive (*3*). Yet, while atrazine has an established maximum contaminant level (MCL) of 3 μg L^{-1} for drinking water in the United States, there are no U.S. standards for atrazine metabolites.

Metabolite concentration data can also be useful in determining the source and pathways of atrazine movement in the environment. The molar concentration ratio of deethylatrazine to atrazine, referred to as DAR, can be used to distinguish point source from nonpoint source contamination of groundwater (*9*) and to measure the timing and movement of atrazine in reservoirs and streams (*10*). Additionally, the ratio of DIA to DEA, referred to as D^2R, can be used in conjunction with the concentrations of the parent compounds to differentiate DIA derived from atrazine from that originating from the breakdown of other triazine herbicides (*11*). Yet, there have been few long-term studies on the losses of atrazine metabolites in surface runoff despite the fact that a comprehensive investigation at 10 Management Systems Evaluation Areas (MSEAs) throughout the U.S. Midwest concluded that surface water is more vulnerable to atrazine contamination than groundwater and that further studies are needed to assess the significance of atrazine and atrazine metabolites in surface water (*12*).

Therefore, our objective was to monitor losses of atrazine, DEA, and DIA in surface runoff from small watersheds farmed using a variety of conservation tillage practices and to evaluate the tillage and climatic factors affecting losses of atrazine and its metabolites, DAR and D^2R.

Experimental Methods

Field. Losses of atrazine, DEA, and DIA in surface runoff from two no-till and two chisel-plowed watersheds in a 2-year corn/soybean rotation and three disked watersheds in a 3-year, reduced-input, corn/soybean/wheat−red clover rotation were monitored year-round for six years (spring 1995 to spring 2001). One watershed in each tillage treatment was planted to each crop each year. All seven watersheds are within 1 km of each other and are part of the network of watersheds maintained by the USDA−ARS for 60+ years at North Appalachian Experimental Watershed near Coshocton, OH. Weighing-type rain gauges positioned near each watershed or group of watersheds were used to record pre-

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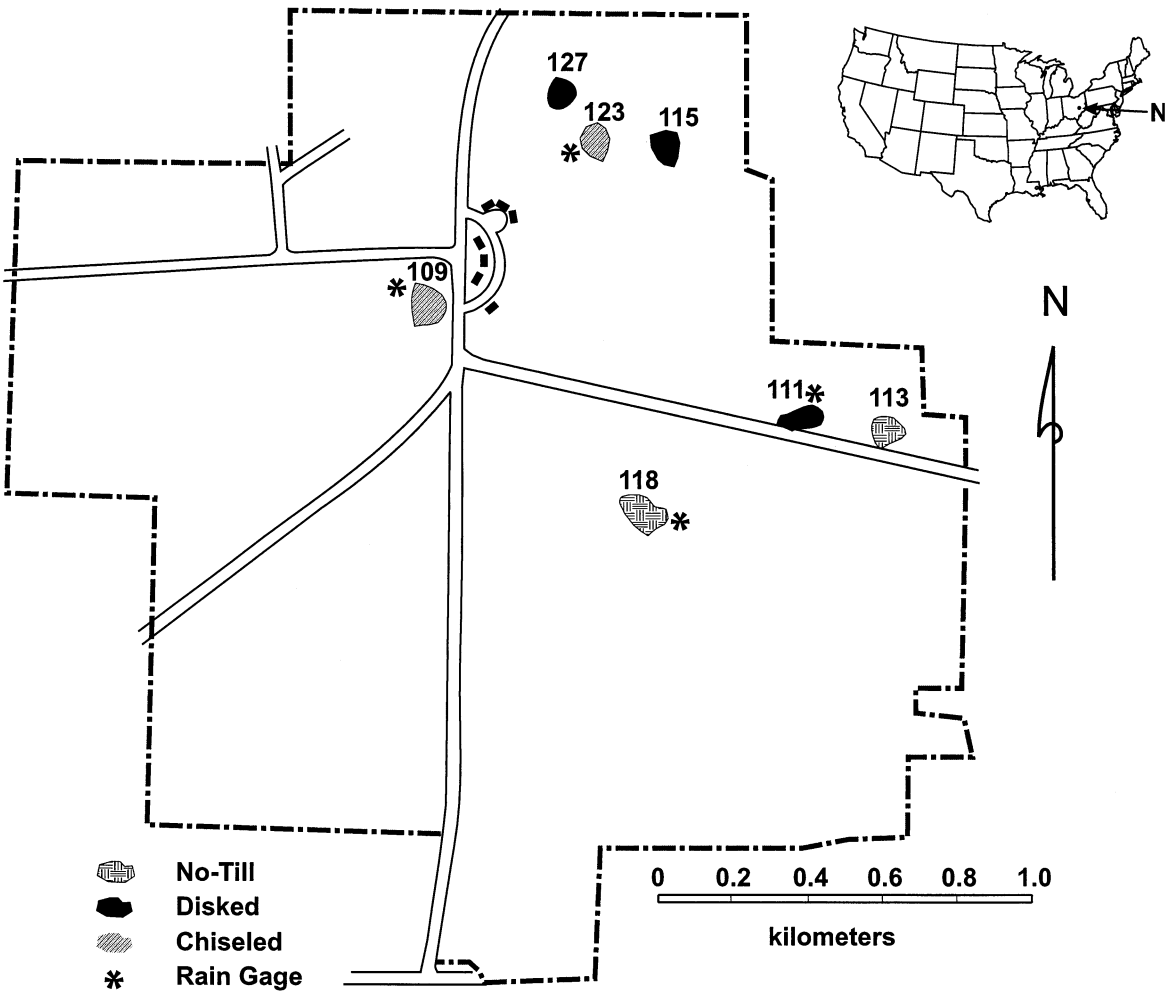

FIGURE 1. Location of the North Appalachian Experimental Watershed and the seven watersheds and four rain gauges used in the study.

TABLE 1. Tillage Treatments and Characteristics of the Seven Watersheds

watershed number	tillage treatment	area (ha)	av slope (%)	max length (m)	dominant soil series[a]
WS 109[b]	chiseled	0.68	13	110	Rayne sil
WS 123	chiseled	0.55	7	107	Keene sil
WS 113[b]	no-till	0.59	11	118	Coshocton sil
WS 118	no-till	0.79	10	132	Coshocton sil
WS 111	disked	0.45	6	143	Keene sil
WS 115[b]	disked	0.65	7	119	Coshocton sil
WS 127	disked	0.67	9	104	Coshocton sil

[a] Taxonomic classication: Rayne, fine-loamy, mixed, active, mesic Typic Hapludult; Keene, fine-silty, mixed, mesic Aquic Hapludalf; Coshocton, fine-loamy, mixed, mesic Aquultic Hapludalf. [b] Low runoff-producing watershed based on historical records.

cipitation (Figure 1). General characteristics and tillage treatments of the watersheds are outlined in Table 1.

Tillage treatments were assigned to the watersheds based on long-term hydrologic records with one watershed in each tillage treatment having a history of less than average runoff production. Consequently, statistical comparisons among tillage treatments were not performed. Chiseling was carried out shortly before planting, and no secondary tillage operations were conducted on these watersheds. The no-till and chisel-plowed watersheds received a broadcast spray application of atrazine at the maximum labeled rate of 2.24 kg a.i./ha when planted to corn. The disked watersheds were tilled to a depth of ~10 cm three to four times prior to planting in corn and soybean years and received a half-rate, broadcast spray application of atrazine (i.e., 1.12 kg a.i./ha) when sown to corn. After herbicide application these watersheds were usually cultivated between the rows once in June and once in July for additional weed control. Tillage and planting operations were performed along the contour of all the watersheds. The crop management practices on the watersheds were identical to those during the study for a minimum of 5 years prior the beginning of the experiment. During this period and throughout the study, no other herbicides that would yield DEA or DIA as breakdown products were applied to the watersheds.

Runoff volumes were measured using H flumes housed within enclosures that permitted year-round operation of the watersheds (*13*). Data loggers were used to record the hydrographs and activate ISCO samplers equipped with stainless steel strainers, Teflon suction lines, and glass sample bottles. Up to 28 samples per watershed were obtained each time runoff occurred. During runoff, the samplers collected discrete samples every 10 min for the first 100 min, every 20 min for the next 200 min, and every 60 min thereafter until the capacity of the samplers was reached or runoff ceased.

Generally, at the beginning of the crop year, all collected samples were analyzed. As herbicide concentrations in the runoff declined during the year, only samples representative of the beginning, peak, and tail of the hydrograph of each event were analyzed. Flow-weighted average concentrations for each runoff event were computed using the concentrations measured in individual samples and runoff volumes obtained from the hydrographs. When runoff occurred over

TABLE 2. Precipitation, Number of Runoff Events, Percent of Rainfall, and Losses of Atrazine, DEA, and DIA in Runoff[a]

crop year	crop	rainfall (mm)	runoff		% of applied[b]			
			no. of events	% of rainfall	atrazine	DEA	DIA	total
				WS 109 Chiseled				
1995	soybean	865	6	1.5	tr	0.0001	nd	0.0001
1996	corn	1052	8	1.3	0.0075	0.0026	0.0011	0.011
1997	soybean	918	15	0.2	0.0007	0.0006	0.0002	0.0016
1998	corn	866	8	0.2	0.0026	0.0011	0.0004	0.0041
1999	soybean	912	10	0.1	tr	tr	nd	tr
2000	corn	892	5	0.3	0.0002	0.0005	0.0001	0.0008
				WS 123 Chiseled				
1995	corn	1071	25	16.6	2.49	0.10	0.022	2.62
1996	soybean	960	21	12.2	0.0033	0.0048	0.0003	0.0084
1997	corn	1042	25	16.2	2.10	0.25	0.090	2.45
1998	soybean	895	17	17.6	0.028	0.0098	0.0001	0.038
1999	corn	956	8	8.6	0.0071	0.015	0.0064	0.029
2000	soybean	854	8	10.1	0.0023	0.0022	tr	0.0045
				WS 113 No−Till				
1995	soybean	931	25	5.6	0.0026	0.0029	tr	0.0055
1996	corn	1087	35	4.5	0.44	0.045	0.016	0.50
1997	soybean	959	27	6.4	0.015	0.0053	tr	0.020
1998	corn	893	24	7.3	0.65	0.12	0.050	0.82
1999	soybean	939	15	3.9	0.0019	0.0008	nd	0.0027
2000	corn	878	35	5.5	0.68	0.089	0.041	0.81
				WS 118 No−Till				
1995	corn	1116	63	14.0	4.71	0.18	0.067	4.95
1996	soybean	982	52	8.4	0.0022	0.0026	0.0001	0.0049
1997	corn	1074	46	12.1	2.72	0.29	0.11	3.12
1998	soybean	925	42	14.6	0.0052	0.0063	0.0016	0.013
1999	corn	973	37	6.3	0.014	0.017	0.0052	0.036
2000	soybean	885	47	9.9	0.0027	0.0022	tr	0.0050
				WS 111 Disked				
1995	wheat	1091	37	13.1	0.0038	0.0022	0.0002	0.0063
1996	corn	887	26	10.6	0.51	0.11	0.017	0.64
1997	soybean	1051	29	16.6	0.029	0.061	0.0049	0.095
1998	wheat	877	24	16.0	0.0012	0.0017	0.0004	0.0034
1999	corn	940	14	9.4	0.0074	0.028	0.0074	0.043
2000	soybean	971	21	6.9	0.0024	0.0017	0.0001	0.0041
				WS 115 Disked				
1995	corn	1165	37	5.6	0.47	0.099	0.023	0.59
1996	soybean	928	30	5.4	0.0005	0.0005	tr	0.0010
1997	wheat	934	20	4.5	0.0015	0.0015	tr	0.0031
1998	corn	895	19	3.7	0.27	0.20	0.06	0.52
1999	soybean	977	23	7.4	0.0020	0.0007	nd	0.0027
2000	wheat	840	33	8.4	0.0005	tr	nd	0.0006
				WS 127 Disked				
1995	soybean	914	51	21.0	0.0055	0.0035	tr	0.0091
1996	wheat	960	56	9.5	0.0018	0.0017	0.0008	0.0043
1997	corn	1042	42	18.0	4.34	1.66	0.37	6.37
1998	soybean	950	36	22.0	0.015	0.025	0.0072	0.047
1999	wheat	877	24	17.7	0.0047	tr	nd	0.0047
2000	corn	885	23	13.5	0.78	0.31	0.071	1.17

[a] DEA and DIA losses are expressed as a percentage of the parent atrazine and losses in other than corn crop years are based the previous application of atrazine. [b] tr, trace <0.0001%; nd, not detected.

a prolonged period of time in the winter and early spring, and in instances when the automated samplers failed to operate properly, flow-proportional composite samples were obtained using Coshocton Wheel samplers (*13*).

Analytical Methods. Atrazine, DEA, and DIA were extracted from unfiltered runoff samples using LC-18 solid-phase extraction tubes. An internal standard was added to the prepared extracts and they were analyzed using a capillary gas chromatograph equipped with a thermionic-specific detector. Each sample was run on two capillary columns of dissimilar polarity (*14*). When the concentrations differed, the lower value was used on the assumption that the higher value was due to positive interference by other compounds; thus the estimated losses are conservative. The amount of sample extracted increased from 1 to 40 mL as herbicide concentrations decreased with time after application. The minimum detection limits were 0.03 μg L^{-1} for atrazine and 0.06 μg L^{-1} for DEA and DIA.

Results and Discussion

General Observations. The timing of field operations varied from year to year as dictated by weather conditions. In an individual crop year, however, herbicide applications to the no-till and chiseled watersheds were made on the same date, whereas the date of application on the disked watersheds was somewhat delayed in most years to allow for extra time and suitable soil conditions necessary to complete the additional tillage operations these watersheds received.

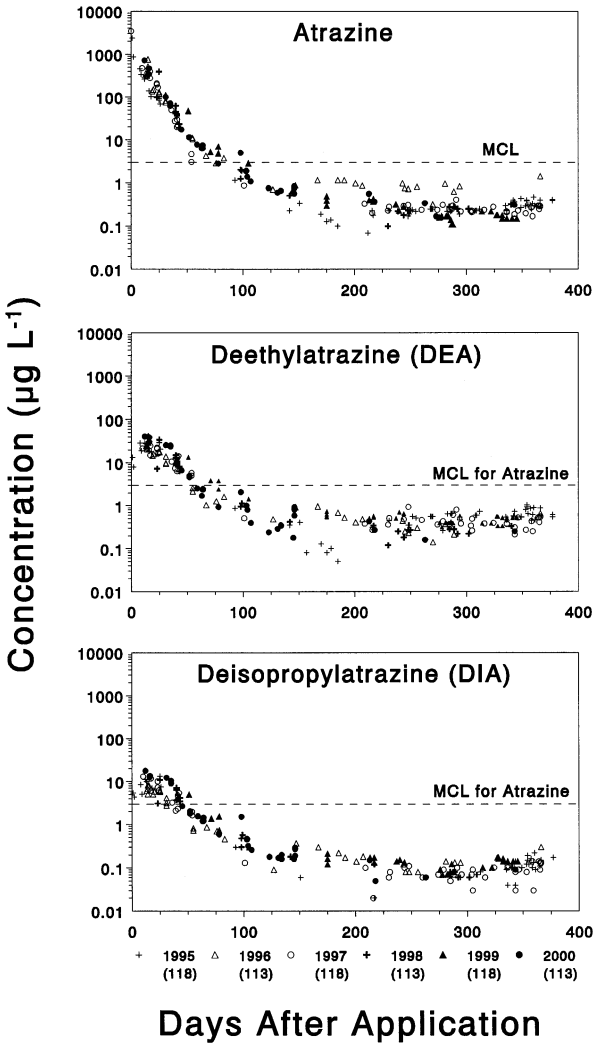

FIGURE 2. Temporal variation of atrazine, deethylatrazine, and deisopropylatrazine concentrations in the two no-till watersheds (WS 113, WS 118) for the six crop years 1995−2000.

Therefore, to compare the runoff, rainfall, and atrazine losses among tillage treatments and years the crop year was defined as beginning on the day of herbicide application and ending with herbicide application the following year. Consequently, variations in precipitation totals among watersheds within years (Table 2) were attributable to variations in crop year ending and starting dates as well as slight differences in actual precipitation at each site.

The general pattern of atrazine, DEA, and DIA concentrations with days after application observed for the no-till watersheds in the corn year (Figure 2) was similar to that for the other tillage treatments (data not shown). The concentration of atrazine was highest when runoff occurred shortly after application and declined sharply with time, regardless of tillage treatment. In contrast, DEA and DIA concentrations were relatively low if runoff occurred shortly after atrazine application and peaked about 25 days after application (Figure 2). As a consequence, atrazine, DEA, and DIA losses in surface runoff varied considerably among watersheds and years as a result of variation in rainfall timing and amounts (Table 2).

Atrazine and Metabolite Transport. The greatest loss of atrazine observed during the study (4.71%) was in 1995 on no-till WS 118 (Table 2). This loss was largely the result of a rainstorm on 18 May, 2 days after atrazine application, that accounted for only 3% of the yearly rainfall and 6% of the yearly runoff yet produced 78% of the yearly atrazine loss. In contrast, in 1999 when corn was also grown on this watershed and the first runoff occurred 51 days after atrazine application, yearly losses were only 0.014% of the applied atrazine. The greatest loss of DEA (1.66%) and DIA (0.37%), as well as the greatest loss of atrazine plus metabolites (6.37%), occurred in 1997 on the disked WS 127. In this instance, the first runoff-producing storm occurred 17 days after atrazine application and produced 4% of the yearly rainfall and 8% of the yearly runoff and accounted for 38% and 37% of the yearly DEA and DIA losses, respectively. These observations further highlight the fact that the timing of rainfall and runoff relative to atrazine application can have a much greater effect

TABLE 3. Flow-Weighted, Yearly Average Concentrations of Atrazine, DEA, and DIA and the Ratios of DEA to Atrazine (DAR) and DIA to DEA (D2R)

crop year	crop	concentration (μg L^{-1}) atrazine	DEA	DIA	DAR	D^2R
		WS 109 Chiseled				
1995	soybean	0.01	0.01	nd[b]	1.75	nd
1996	corn	1.20	0.36	0.14	0.35	0.38
1997	soybean	0.67	0.55	0.23	0.94	0.42
1998	corn	3.99[a]	1.42	0.50	0.41	0.35
1999	soybean	0.05	tr[b]	nd	0.05	nd
2000	corn	0.21	0.39	0.08	2.10	0.20
		WS 123 Chiseled				
1995	corn	31.46[a]	1.15	0.22	0.04	0.19
1996	soybean	0.06	0.08	0.01	1.46	0.07
1997	corn	27.86[a]	2.94	0.96	0.12	0.33
1998	soybean	0.40	0.12	tr	0.35	0.01
1999	corn	0.20	0.36	0.14	2.10	0.39
2000	soybean	0.06	0.05	tr	0.93	nd
		WS 113 No−Till				
1995	soybean	0.11	0.11	tr	1.12	nd
1996	corn	20.07[a]	1.79	0.58	0.10	0.32
1997	soybean	0.55	0.17	tr	0.35	nd
1998	corn	22.44[a]	3.60[a]	1.37	0.18	0.38
1999	soybean	0.12	0.04	nd	0.43	nd
2000	corn	31.48[a]	3.57[a]	1.53	0.13	0.43
		WS 118 No−Till				
1995	corn	67.67[a]	2.25	0.77	0.04	0.34
1996	soybean	0.06	0.06	tr	1.15	0.03
1997	corn	47.00[a]	4.37[a]	1.58	0.11	0.36
1998	soybean	0.09	0.09	0.02	1.23	0.24
1999	corn	0.50	0.54	0.15	1.23	0.28
2000	soybean	0.07	0.05	tr	0.84	0.01
		WS 111 Disked				
1995	wheat	0.03	0.02	tr	0.59	0.10
1996	corn	6.09[a]	1.14	0.16	0.22	0.14
1997	soybean	0.18	0.34	0.03	2.13	0.07
1998	wheat	0.01	0.01	tr	1.37	0.23
1999	corn	0.09	0.31	0.08	3.80	0.24
2000	soybean	0.04	0.02	tr	0.70	0.06
		WS 115 Disked				
1995	corn	7.99[a]	1.47	0.31	0.21	0.21
1996	soybean	0.01	0.01	tr	0.97	0.03
1997	wheat	0.04	0.04	tr	1.00	0.01
1998	corn	9.38[a]	5.83[a]	1.52	0.71	0.26
1999	soybean	0.03	0.01	nd	0.36	nd
2000	wheat	0.01	tr	nd	0.10	nd
		WS 127 Disked				
1995	soybean	0.03	0.02	tr	0.63	0.01
1996	wheat	0.02	0.02	0.01	0.96	0.40
1997	corn	25.83[a]	8.60[a]	1.77	0.38	0.21
1998	soybean	0.08	0.12	0.03	1.67	0.27
1999	wheat	0.03	tr	nd	0.01	nd
2000	corn	7.30[a]	2.55	0.54	0.40	0.21

[a] Flow-weighted yearly average concentrations of atrazine and deethylatrazine that exceed the MCL for atrazine. [b] nd, not detected; tr, trace <0.0001%.

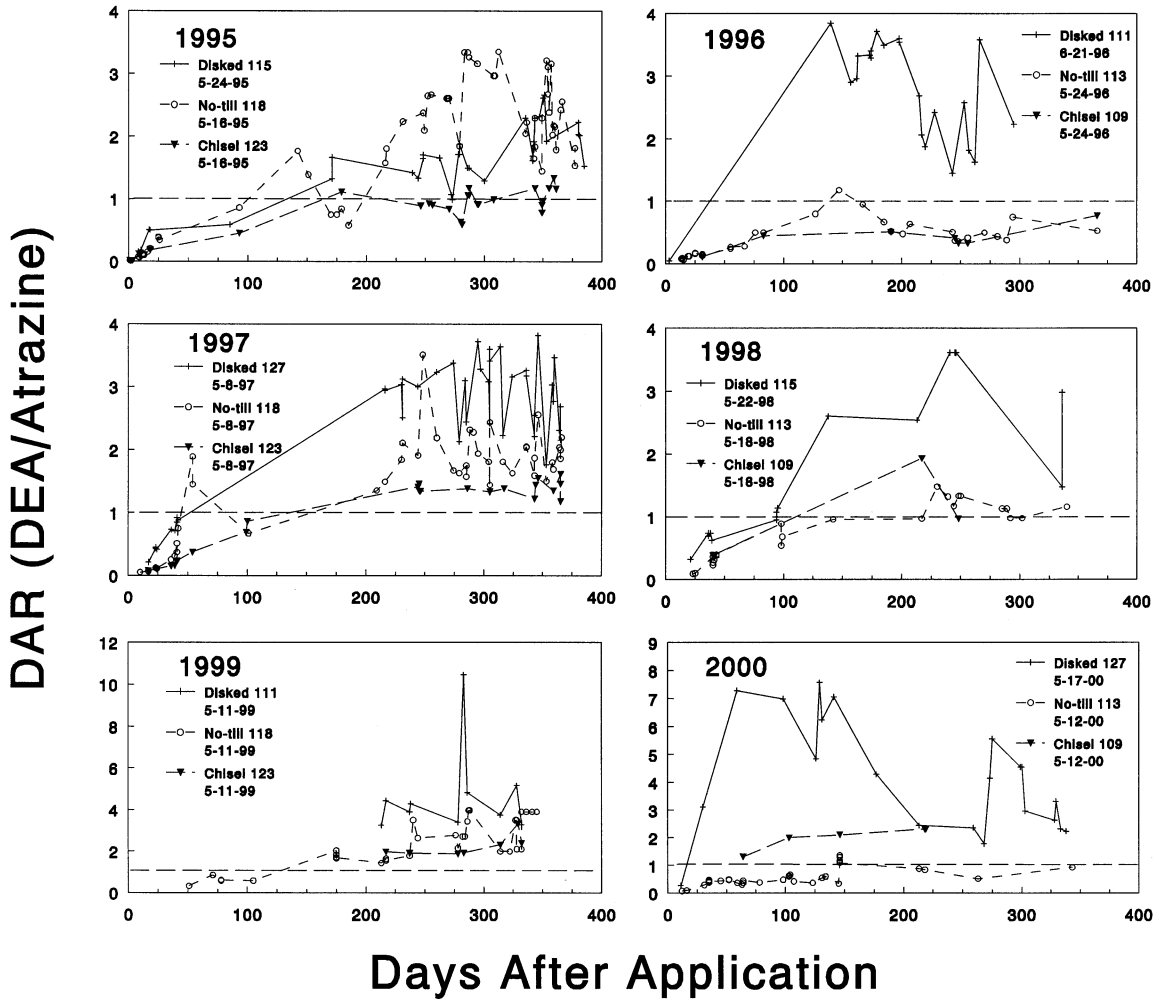

FIGURE 3. Temporal variation of the deethylatrazine/atrazine molar concentration ratio (DAR) in the corn crop year for all seven watersheds. Date of atrazine application for each watershed noted in the figure legends.

on the yearly losses of the parent compound and these two metabolites than the agronomic management practices investigated.

In most crop years, atrazine losses in runoff exceeded that of either of the two metabolites. In 12 of the 42 watershed years investigated, however, DEA losses exceeded those of atrazine (Table 2). For the most part, these were crop years following corn except for WS 109 in 2000 and WS 111, WS 118, and WS 123 in 1999. These were corn years in which there was generally less than average runoff and few runoff events shortly after atrazine was applied. In all 12 cases, these were years in which total losses (i.e., atrazine plus DEA and DIA) were low, <0.1% atrazine equivalent. Losses of DIA were always less than that of atrazine or DEA, and in six crop years, all following corn, no DIA was detected in runoff. In contrast, atrazine and DEA were noted in runoff in all crop years, even in the disked watershed in the wheat crop year, 2 years after atrazine application.

Atrazine and Metabolite Concentrations. Atrazine concentrations generally exceeded the 3 μg L^{-1} MCL when runoff occurred <100 days after application (Figure 2). The highest concentration noted for an individual event was 3452 μg L^{-1} and was the result of runoff from WS 118 in 1997 on the day of application. Of the 480 runoff events during the corn year, atrazine was above its detection limit of 0.03 μg L^{-1} for all but eight events and these tended to be the result of small runoff events late in the crop year. Flow-weighed, yearly average concentration of atrazine exceeded the MCL at least one corn crop year in all seven watersheds (Table 3). In subsequent crop years, atrazine concentrations in individual runoff events never exceeded the MCL and flow-weighted yearly average concentrations ranged from 0.01 to 0.67 μg L^{-1} (Table 3). In a previous study, however, a few instances where atrazine concentrations exceeded the MCL in runoff events during the soybean crop year were noted in some of these watersheds (*15*). In the soybean crop years, atrazine was detected in 74% of the 475 runoff events. In wheat crop years, atrazine detection dropped to 37% of the 194 runoff events.

DEA concentrations, with few exceptions, were higher than those of DIA in all runoff events. The highest DEA concentration noted was 49 μg L^{-1} and was the result of runoff 23 days after atrazine application to WS 127 in 1997. This concentration was comparable to the maximum of 52 μg L^{-1} DEA reported in surface runoff from plots in Ontario (*16*). The highest DIA concentration noted was 18 μg L^{-1}, 12 days after atrazine application to WS 113 in 2000. Concentrations of DEA and DIA above the MCL for atrazine were usually observed up to ~50 days after application (Figure 2). Flow-weighed, yearly average concentration of DEA exceeded the atrazine MCL in 5 of the 18 corn crop years (Table 3). Both metabolites were above the detection limit of 0.06 μg L^{-1} for most of the 480 runoff events (DEA 467, DIA 417) during the corn years. In subsequent crop years, both metabolites were less frequently detected and the concentrations for individual events never exceeded the MCL for atrazine. DEA detections in individual runoff events dropped to 65% in the soybean years and 28% in the wheat years, and

DIA detections dropped to 9% in the soybean years and 14% in the wheat years.

The European Community (EC) drinking water standard for atrazine and its metabolites is 0.1 μg L^{-1} (*17*), the same concentration at which atrazine reportedly affects the sexual development of frogs (*6*, *7*). The flow-weighted yearly average concentrations of all three compounds exceeded the EC standard in all but 2 of the 18 corn crop years (Table 3). For all 1149 individual runoff events recorded during the study, atrazine and DEA exceeded 0.1 μg L^{-1} in more than half the events (atrazine 53%, DEA 58%) whereas DIA was above this level in 29% of the time. Perhaps more importantly, however, atrazine concentrations during corn years greatly exceeded this level in the spring (Figure 2) when amphibians are breeding and are at greatest risk (*7*).

Metabolite Ratios. DEA, although only a minor breakdown product of atrazine, is less strongly sorbed than atrazine, and thus is more mobile in most soils (*10*). If atrazine movement through soil occurs slowly, which would allow time for degradation to occur, the water should be enriched in DEA relative to atrazine. Consequently, it has been proposed that point versus nonpoint contamination of groundwater can be distinguished based on the molar ratio of DEA to atrazine (DAR) with ratios <1 indicative of point source contamination, as might be found when relatively little degradation occurs during transport due to a spill or entry via a well. Ratios of >1 signify that substantial degradation has occurred during transport, thus a nonpoint source. In streams and reservoirs, a rapid drop in DAR has been noted coincident with the springtime application of atrazine to corn fields and the first major runoff event (*10*). Thus, DAR may also be useful in tracing movement of nonpoint sources of atrazine through surface water bodies.

The yearly average flow-weighted DAR values for the watersheds provided little useful information as the values were highly dependent on the volume of flow as well as timing of the runoff events, among other factors (Table 3). While one would expect the DAR to be lower in corn crop years than in the succeeding crop years, this was often not the case for the reasons indicated above. In addition, during noncorn years when atrazine and DEA concentrations were near their detection limits, the DAR values exhibited high variability among events resulting from the increased relative analytical error associated with these values (*9*). On the other hand, the variation in DAR with days after application during corn years was somewhat more informative. DAR generally increased with time after atrazine application (Figure 3). DAR values of >1 usually did not occur until 100 days after application. In all corn crop years, except for 1995, the DAR values for the disked watersheds, which received a half rate of atrazine and were cultivated after herbicide application, tended to be higher than those for the no-till and chisel-plowed watersheds. Thus, partial incorporation of the surface-applied atrazine during cultivation may have increased the rate of metabolite formation or increased the transport of DEA relative to atrazine compared to the conservation tillage systems where no mechanical incorporation occurred. In leaching studies, no-till was found to attenuate loadings of DEA resulting in lower DAR values compared to conventional tillage, possibly due to greater near-surface organic carbon and soil water content in the no-till soil (*18*).

In the corn crop year of 1996, for the chisel-plowed WS 109, and in 1996 and 2000, for the no-till WS 113, the DAR values were rarely if ever >1 while the values for the disked watersheds were substantially >1 for all runoff events except the first one after application (Figure 3). This suggests that there may be an interaction between tillage treatment and weather year that affects DAR. Coincidently, the DAR values for the high-runoff-producing counterparts of the chisel-tilled WS 109 and no-till WS 113, WS 123 and WS 118,

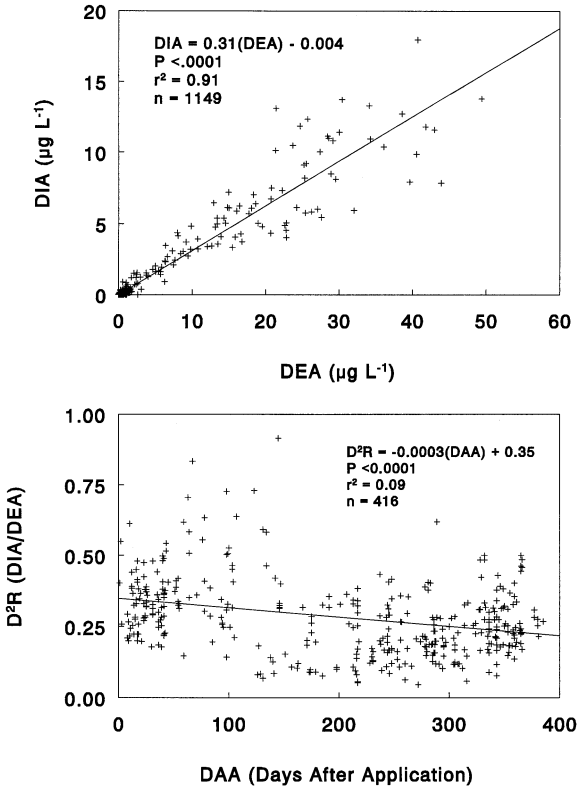

FIGURE 4. Relationship of deisopropylatrazine to deethylatrazine concentration for all runoff events and temporal variation in the deisopropylatrazine/deethylatrazine ratio (D^2R) for the corn crop years.

respectively, behaved more typically in all weather years with DAR generally increasing with time to values of >1 during the corn crop year (Table 1 and Figure 3). These two watersheds are more poorly drained than WS 109 and WS 113, and lateral flow within these watersheds contributes to the increased surface runoff observed. It has been suggested that increased contribution of lateral flow and leaching to surface flow should increase DAR (*10*). Regardless, the data suggest that tillage treatment, soil type, and weather year can all affect DAR. These factors may need to be taken into account when DAR is used as an index of atrazine movement in streams and when DAR is used to distinguish point from nonpoint sources of atrazine contamination.

To use the concentration ratio of DIA to DEA (D^2R) to determine the fraction of nonpoint contamination of water with DIA arising from the use of atrazine versus other triazine herbicides that yield DIA as a metabolite, a relatively constant ratio of DIA to DEA is assumed when atrazine is the sole source of DIA (*11*). Linear regression of the flow-weighted DIA and DEA concentrations for all runoff events for all crop years indicated a strong relationship ($r^2 = 0.91$) with DIA concentration, about 31% of DEA concentration (Figure 4). Thus, DIA concentrations were slightly lower relative to DEA than those reported in other studies of surface runoff from atrazine-treated plots where DIA concentrations were 40% of DEA (*11*, *19*). In a river system, however, DIA concentrations were 52% of DEA, thus somewhat higher than we noted (*10*). The discrepancy in D^2R among studies may be related to differences in analytical methods and metabolite recovery or due to differences in the rate of metabolite production in the soil and river systems investigated. Alternatively, the discrepancy may be related to a change in D^2R with time.

In the plot studies, D^2R was only measured for a relatively short time after application whereas we measured DIA and DEA concentrations year round. While a significant relation-

ship between D^2R and days after application was not detected when all crop years were considered (data not shown), this due to the fact that both DIA and DEA were near or below their detection limits in soybean and wheat crop years and D^2R was rarely defined for individual runoff events during these crop years. This was reflected in the yearly flow-weighted average D^2R values, which were not defined in 9 of the 24 soybean and wheat crop years and ranged from 0.01 to 0.42 in the remaining noncorn crop years as opposed to the more narrow range of 0.14−0.43 for the corn crop years (Table 3). When only the corn crop year was considered (Figure 4), a significant decline in D^2R with time was noted. Nevertheless, this relationship accounted for only a small fraction of the variability in D^2R ($r^2 = 0.09$) and the decline with time was slight. Therefore, the decline in D^2R with time probably would not be sufficient to affect its usefulness in discriminating among sources of DIA in surface water. The decline in D^2R with time was likely the result of more rapid breakdown of DIA compared to DEA as was noted in a study of the persistence of atrazine metabolites in a reservoir (*20*).

Acknowledgments

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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